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Communication

Green, safe, fast, and inexpensive removal of CO_2 from aqueous $KHCO_3$ solutions using a nanostructured catalyst $TiO(OH)_2$: A milestone toward truly low-cost CO_2 capture that can ease implementation of the Paris Agreement

Sam Toan[a,f,1], Qinghua Lai[a,1], William O'Dell[a], Zhao Sun[a], Huiping Song[b], Ying Zhao[a], Maciej Radosz[a], Hertanto Adidharma[a], Christopher Russell[e], Hongbao Yao[c], Yujun Wang[c], Weiyang Fei[c], Maohong Fan[a,d,*]

[a] College of Engineering & Applied Science, University of Wyoming, Laramie, WY, USA
[b] Institute of Resources and Environmental Engineering, Shanxi University, Taiyuan 030006, China
[c] State Key Laboratory of Chemical Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China
[d] School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, USA
[e] Department of Civil & Environmental Engineering, Stanford University, Stanford, CA, USA
[f] Department of Chemical and Environmental Engineering, University of California, Riverside, CA, USA

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ABSTRACT

With great effort, the Paris Agreement set goals designed to address climate change, but far more effort will be necessary to meet those goals due to the lack of transformational CO_2 capture technologies that are cost-effective. This research is designed to overcome the shortcomings of conventional CO_2 capture technologies (i.e. the cost, health impacts, and environmental impacts of amines) by using a titanium oxyhydroxide ($TiO(OH)_2$) catalyst and a potassium carbonate/bicarbonate sorbent (K_2CO_3/$KHCO_3$, respectively). Nanostructured $TiO(OH)_2$ as a catalyst is able to accelerate desorption processes; the acceleration of CO_2 desorption is of greater significance because the process consumes more energy than the sorption process. Experimental results show that the use of nanostructured $TiO(OH)_2$ increases the amounts of desorbed CO_2 by as much as 1200%, if not higher. Cyclic sorption-desorption testing combined with material characterization shows that both catalyst and sorbent are stable even after 50 cycles. One major benefit of the kinetic enhancement from this catalyst/sorbent system is the reduction of temperature needed to desorb CO_2; waste heat may be sufficient to provide all or most of the energy required for CO_2 capture. Thus, the energy cost of CO_2 capture will be significantly reduced, which may keep electricity prices low, avoiding a decrease in the global economy in order to avert global climate change impacts. Another significant benefit of this system is that this inorganic system is environmentally safe, clean, and non-carcinogenic.

1. Introduction

Reducing the cost of carbon dioxide (CO_2) separation from fossil fuel flue-gas is the primary challenge of reducing climate change inducing CO_2 emissions, which will help meet the goals set at the Paris Climate Accord [1]. Common CO_2-separation technologies, such as sorption in amine or carbonate solutions, are reliable, but are energy intensive and thus costly [2–4], accounting for over 80% of the total capture, transportation, and storage cost [5]. What is it that makes it so expensive? It's the CO_2 desorption alone! During a sorption step, CO_2 readily and selectively bonds to the separation agent, such as amine or carbonate, but for the same reason it bonds with the separation agent, it is slow to break the bond during a desorption step to recover the sorbent. This is precisely why the known CO_2 desorption technologies are so expensive: they have to provide plenty of energy to break the CO_2-sorbent bond, often requiring temperatures above 100 °C to increase the rate of desorption [6]. Unfortunately, such temperatures are too high for easy integration with existing low-cost, waste-heat energy sources.

* Corresponding author at: College of Engineering & Applied Science, University of Wyoming, Laramie, WY, USA.
E-mail addresses: mfan@mail.gatech.edu, mfan@uwyo.edu (M. Fan).
[1] Equal Contribution.

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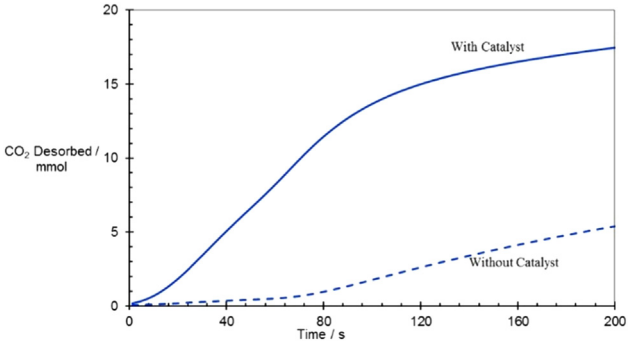

Fig. 1. CO_2 desorption over time both $TiO(OH)_2$ catalyst drastically increases the rate of CO_2 desorption from $KHCO_3$. (Initial $KHCO_3$ concentration: 10 wt%; $TiO(OH)_2$ concentration: 3 wt%; reaction temperature: 60 °C; N_2 flowrate: 500 mL/min).

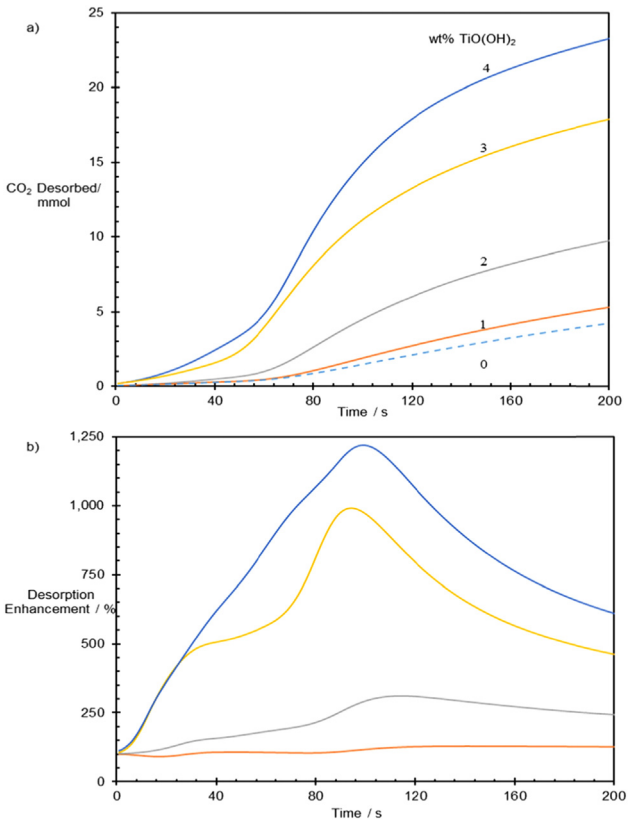

Fig. 2. The increase in CO_2 desorbed on a) quantity and b) percent bases due to the concentration of catalyst in the system (initial $KHCO_3$ concentration: 10 wt %; nanostructured $TiO(OH)_2$ concentrations: 0–4 wt%; CO_2 desorption temperature: 60 °C; N_2 flowrate: 500 mL/min).

Such temperatures can also decompose amines causing costly sorbent losses, not to mention toxic, carcinogenic emissions of decomposition by-products [7].

Energy production has created a need for large scale CO_2 capture technology optimization and the undesirable effects of CO_2 being emitted into the atmosphere can no longer be overlooked. Many technological advances have been discovered and utilized to reduce SO_x/NO_x and Hg emissions released due to the burning of fossil fuels, but CO_2 capture technology remains in a developmental stage. Global steps have been taken to reduce CO_2 emissions and ultimately attain the goal set by the Paris Agreement, which is to hold the increase of global temperatures under 2 °C above pre-industrial global temperatures [1].

CO_2 capture has been tested using different technologies, such as

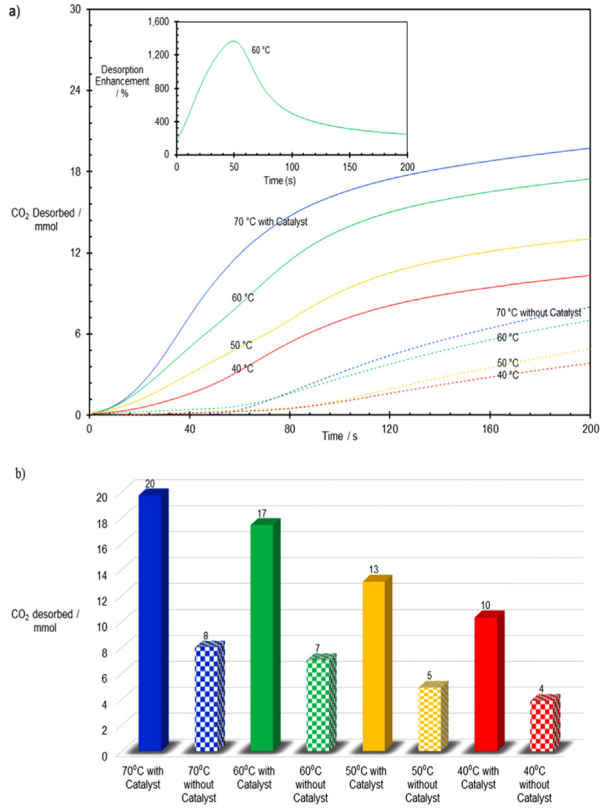

Fig. 3. a) The increase in CO_2 desorbed at various temperatures. b) The percent enhancement of the rate of desorption at 60 °C. (initial $KHCO_3$ concentration: 10 wt%; $TiO(OH)_2$ concentration: 3 wt%; reaction temperature: 40–70 °C; N_2 flowrate: 500 mL/min).

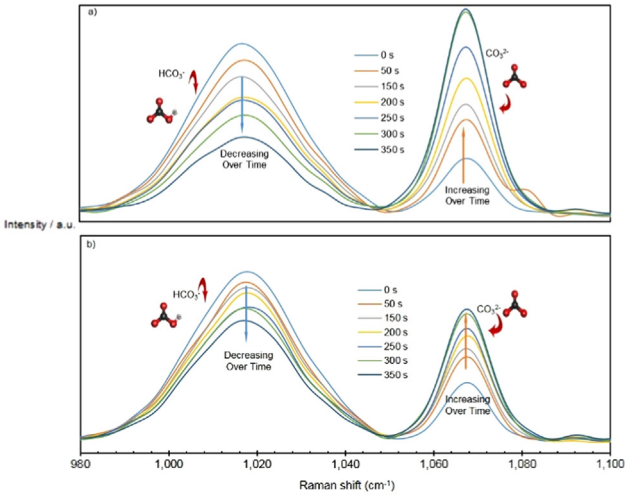

Fig. 4. Raman spectra of (a) catalyzed and (b) uncatalyzed CO_2 desorption at different desorption times confirm the effectiveness of the titanium oxy hydroxide catalyst.

the use of solid sorbents, solvents, and membrane capture techniques, many of which could possibly be implemented to reduce CO_2 emissions on a large scale [8]. Solid amine sorbents [9] and membrane capture techniques [10] were implemented and studied, but proved to be inefficient and uneconomically. On the other hand, aqueous phase sorbent technology was first used in the 1930s for the separation of CO_2 from produced natural gas in oil fields [8,11].

The two main types of CO_2 capture-based sorbents used are inorganic and organic, with the organic-based CO_2 capture methods being

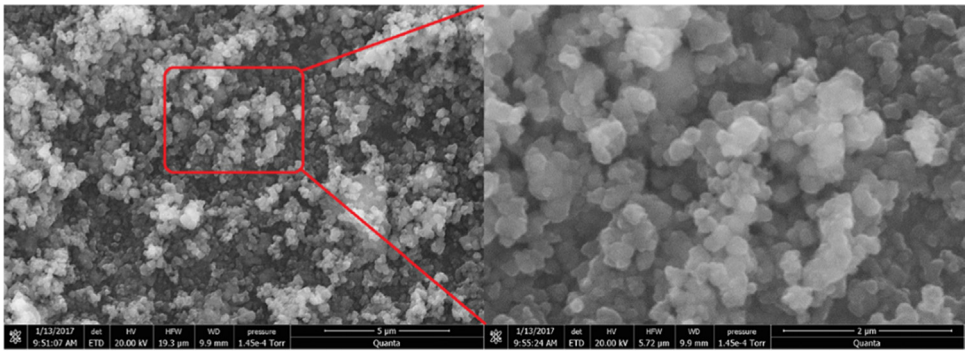

Fig. 5. SEM images of fresh nanostructured $TiO(OH)_2$ samples.

Table 1
BET characteristics of fresh $TiO(OH)_2$.

Catalyst	BET surface area (m^2/g)	Pore volume (cm^3/g)
Fresh $TiO(OH)_2$	819.8	0.804
Used $TiO(OH)_2$	782.9	0.783

the least cost effective due to high decomposition rates and toxicity. Inorganic aqueous sorbents are much more cost effective and have been shown to be suitable sorbents for CO_2 extraction through the Benfield Process, [11,12] however, the desorption process for inorganic sorbents is very energy intensive.

The single most important question therefore is this: how can the rate of CO_2 desorption be increased at lower temperatures? A simple answer demonstrated in this work for potassium bicarbonate, $KHCO_3$, is to use a suitable catalyst [12], for example an inexpensive nanostructured $TiO(OH)_2$ catalyst. Whereas previous study has demonstrated the viability of this catalyst across 5 cycles while regenerating the catalyst between each cycle,[12] we aim to demonstrate the stability of the catalyst over 50 cycles without catalyst regeneration between each.

2. Catalytic rate enhancement

Just how drastic such a catalytic rate enhancement can be is illustrated with a sample of data shown in Fig. 1 for a desorption experiment using a 10 wt% water solution of $KHCO_3$, 3 wt% nanostructured $TiO(OH)_2$, and a model nitrogen carrier at 60 °C. The enhancement measured with a relative difference in desorbed CO_2 after 200 s is found to be as much as 360%. More detailed data, all consistently pointing to a substantial enhancement, albeit expectedly lower at lower carrier flow rates, are shown in Fig. S1. What if we change the catalyst concentration?

2.1. Effect of catalyst concentration

As expected, the quantity of desorbed CO_2 increases with increasing nanostructured $TiO(OH)_2$ concentration, as shown in Fig. 2a. The inset brings out a percent catalytic enhancement, measured as a percent ratio of the desorption rate with the catalyst to that without the catalyst, which reaches over 1200% at its peak for a catalyst concentration of 4 wt% (See Fig. 2b). We therefore select this concentration as our new benchmark, which will have to be optimized in the future. While higher catalyst concentrations may result in higher enhancements, they are not considered due to preliminary economic considerations.

2.2. Effect of reaction temperature

As for the desorption process, in general, higher temperatures are expected to favor higher desorption rates, as shown in Fig. 3. For example, the quantity of CO_2 catalytically desorbed in 200 s at 40 °C is 10 mmol, which means an enhancement of 285% relative to that without nanostructured $TiO(OH)_2$ at the same temperature. At 60 °C, the corresponding enhancement is 248%. As directionally shown in the Fig. 3 inset at 60 °C, the catalytic desorption enhancements go through a peak of 1300% and then, consistent with thermodynamic analysis, gradually decrease with time. Although higher temperatures can result in somewhat higher enhancements, the important learning is that relative low temperatures, say up to 60 °C, can suffice for rapid CO_2 desorption. For example, at 100 s, the quantity of desorbed CO_2 at 40 °C is twice that at 70 °C.

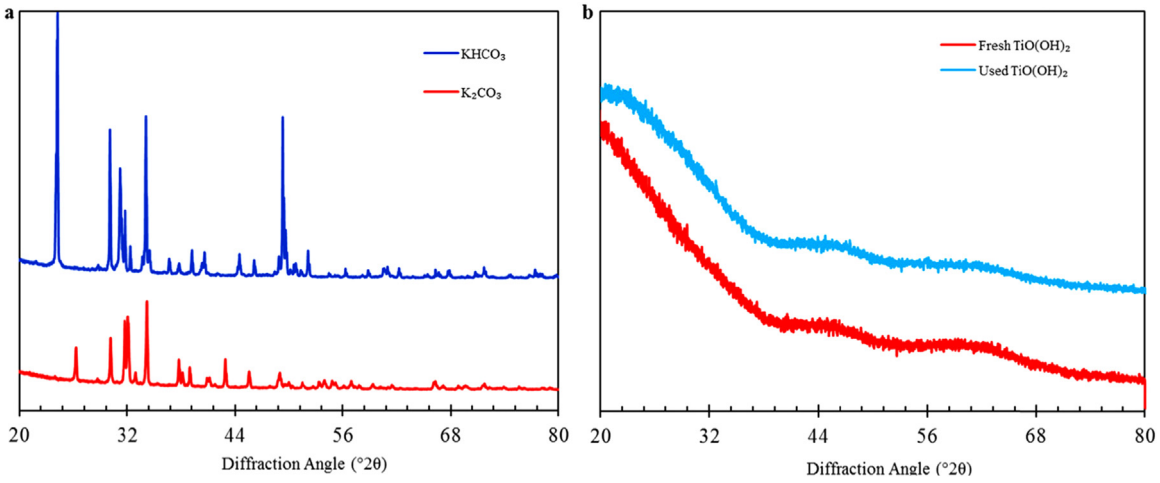

Fig. 6. XRD patterns of $KHCO_3$, K_2CO_3, fresh nanostructured $TiO(OH)_2$, and used nanostructured $TiO(OH)_2$ samples.

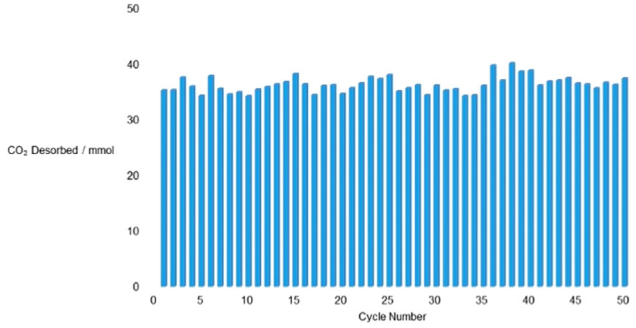

Fig. 7. The quantity of desorbed CO_2 remains relatively stable upon multiple catalyst regeneration cycles. (initial $KHCO_3$ concentration: 10 wt%; $TiO(OH)_2$ concentration: 4 wt%; absorption temperature: 25 °C; N_2 flowrate: 900 mL/min; CO_2 flowrate: 100 mL/min; desorption temperature: 25–65 °C; N_2 flowrate: 500 mL/min; absorption duration: 30 mins; desorption duration: 20 mins).

3. Material analysis

3.1. Raman spectrometry analysis

The catalytic desorption enhancements are confirmed through Raman spectrometry. The peaks at approximately 1020 cm^{-1} and 1070 cm^{-1} represent HCO_3^- and CO_3^{2-} [13,14], respectively. The peak intensity of HCO_3^- at 1020 cm^{-1} with catalyst decreases at a much higher rate (Fig. 4a) than that without catalyst (Fig. 4b). In addition, the peak intensity at 1070 cm^{-1} indicates that the K_2CO_3 formation rate is significantly higher with catalyst than that without catalyst. The Raman analysis thus also confirms the increased desorption kinetics with catalyst.

SEM images shown in Fig. 5 for fresh nanostructured $TiO(OH)_2$ confirm that the catalyst particles are fine and highly dispersed [15]. The size of the particles is at the nanometer level and thus expected to have a large surface area, as illustrated in the BET characterization data (Table 1). The used $TiO(OH)_2$ BET information shows only a slight decrease in surface area and pore volume. This indicates the great stability of the catalyst.

XRD patterns of K_2CO_3 and $KHCO_3$ in Fig. 6 confirm their characteristic peaks [13,16], while those for the fresh and used nanostructured $TiO(OH)_2$ samples in Fig. 6b confirm no remarkable peak change in the catalyst spectrum and thus its good stability.

The morphologies of fresh and spent catalysts are studied on a scanning electron microscope (SEM, FEI, Quanta 250). The Brunauer-Emmett-Teller surface areas and pore size distribution of nanostructured $TiO(OH)_2$ samples are measured by using a Quantachrome Autosorb-iQ pore structure analyzer. Pore volumes are estimated from the adsorbed amount of N_2 at a relative pressure of 0.99. Raman spectra of the samples are collected on a Raman Sierra IM-52 instrument from Snowy Range Instruments with a 758 nm laser and 3 MW power. Powder X-ray diffraction analyses of catalysts are performed on a Rigaku X-ray diffraction system utilizing Cu Kα1 radiation at 40 kV and 40 mA. Samples are placed on a zero diffraction Si holder and scanned from 5° to 50° (2θ) with a 5 °/min scanning rate at room temperature.

3.2. Cyclic stability

The substantial catalytic enhancements discovered in this work inspire two practical questions: Can they be sustained upon multiple regeneration cycles? How stable can the nanostructured $TiO(OH)_2$ catalyst be? On a realistic lab scale, it is observed that nanostructured $TiO(OH)_2$-catalyzed CO_2 desorption data obtained for aqueous $KHCO_3$ solutions in 50 cyclic regeneration experiments exhibit no significant decrease in the amount of CO_2 desorbed, as shown in Fig. 7. These results suggest that nanostructured $TiO(OH)_2$ and $KHCO_3$ are a very stable catalyst-sorbent pair.

4. Conclusion

An inexpensive titanium oxy hydroxide catalyst is found to drastically enhance the rates of CO_2 removal from potassium bicarbonate: the slowest and the most energy intensive step of carbon capture in liquid carbonate solutions. Such catalytic enhancements can be as high as 1200%, if not higher. This means that the cost of notoriously energy-intensive and thus expensive carbon capture processes can be radically reduced. These technical advantages underpin three economic promises: (1) a much faster desorption means smaller reactors and thus lower capital costs, (2) lower desorption temperatures mean lower energy requirements to break the CO_2-sorbent bond, which most likely can be satisfied by the existing waste-heat energy streams, and (3) the use of inorganic sorbent means fewer, if any, toxic emissions and sorbent losses normally associated with the conventional amine technology, and consequently fewer costs for damage prevention techniques.

5. Material preparation and experimental illustration

Titanium isopropoxide (TTIP), ethanol (EtOH), and potassium bicarbonate (KHCO3) were purchased from Sigma-Aldrich and utilized without any additional purification prior to preparing titanium oxy hydroxide (TiO(OH)2). TiO(OH)2 is prepared by adding 130 mL titanium isopropoxide dropwise to 1800 mL of deionized water at room temperature, and then stirring the mixture continuously for 4 h. The white precipitate that forms is then separated by filtration, and rinsed several times using deionized water and then anhydrous ethanol sequentially. The wet TiO(OH)2 is dried at 120 °C in an oven for more than 12 h.

A series of experiments testing aqueous $KHCO_3$ decomposition are performed using the experimental setup illustrated in Fig. S2. The $KHCO_3$ decomposition test is initiated by adding a specific amount of nanostructured $TiO(OH)_2$ catalyst, along with $KHCO_3$ and deionized water, into the reactor, using temperature control and digital monitoring systems to maintain consistent reaction conditions. During these experiments, N_2 gas is used to carry the desorbed CO_2 out of the reactor through the system to the sensors. A mass spectrometer is used to monitor the effluent concentration from the reactor. The data are recorded and concentration vs. time data are later extracted. Various experiments are performed to investigate parameters that effect the desorption efficiency. These experiments consist of cyclic $KHCO_3$ decomposition tests while varying the ratio of nanostructured $TiO(OH)_2$ and $KHCO_3$, temperature, and reactant flow rates.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2018.09.009.

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